

LIQUEFACTION CO-PROCESSING OF COAL AND SHALE OIL AT LOW SEVERITY CONDITIONS

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ABSTRACT

Results are reported for a series of single stage batch reactor experiments in which Wyodak subbituminous coal and shale oil derived from medium grade Colorado oil shale were co-processed at low severity reaction conditions using $\text{CO}/\text{H}_2\text{O}$ as reducing agent. Distillate yields of over 85 wt% MAF coal with hydrogen equivalent consumptions of about 1.0 wt% MAF coal were obtained at 600°F reaction temperature. Results from blank shale oil runs at the same mild reaction conditions suggested that shale oil residuum reactivity was enhanced in the presence of coal or primary coal-derived products.

INTRODUCTION

The possibility of liquefying coal at low severity reaction conditions ($\leq 700^\circ\text{F}$) has intrigued researchers for many years. As early as 1921, Fischer and Schrader (1) reported production of an ether-soluble material from coal at 660°F using carbon monoxide and water as reducing agent. More recently other groups including the Pittsburgh Energy Technology Center (PETC) (2), the North Dakota Energy Research Center (3-4), SRI (5-7), and Carbon Resources, Inc. (8) have investigated various methods of utilizing H_2 , $\text{CO}/\text{H}_2\text{O}$ or $\text{CO}/\text{H}_2/\text{H}_2\text{O}$ (syngas) in low severity liquefaction processes. Many incentives exist for converting coal at milder reaction conditions. The most important of these are listed below:

- 1) Reduced H_2 (or CO) consumption and hydrocarbon gas make
- 2) Better distillate and residuum product quality, since carbonization and other retrogressive reactions are suppressed to a large extent
- 3) Production of less refractory residuum which is more susceptible to hydrocracking in a conventional second stage hydrotreater or hydrocracker
- 4) Significant energy savings associated with lower operating temperatures
- 5) Less severe slurry handling and materials of construction problems

A number of studies have been reported in which coal and non-coal-derived heavy oil have been co-processed at severe reaction conditions to obtain valuable distillable liquid products (9-11). In some cases, larger distillate yields were obtained by co-processing coal and heavy oil than by processing each feed separately. Shale oil has been identified as a particularly promising feed, due in part to the high heterocyclic basic nitrogen content of the oil (12). In spite of the advantages of operating at milder conditions, little work on low severity co-processing has been reported.

The objective of this paper is to report yield and conversion data from a series of single-stage low severity co-processing runs using Wyodak subbituminous coal and shale oil derived from medium grade Colorado shale. Blank shale oil runs (no coal added) were also completed at low severity conditions to estimate the individual distillate yield contributions of coal and shale oil.

EXPERIMENTAL PROCEDURE

Wyodak subbituminous coal sample Wyo-3 was used as feed coal in the low severity liquefaction co-processing experiments. The ultimate analysis for this sample is presented in Table I. Sampling and preparation details of the coal have been reported elsewhere (13,14). Previous reactivity studies performed on four Wyodak subbituminous coals including Wyo-3 indicated that Wyo-3 was an extremely reactive coal at representative direct liquefaction reaction conditions (13,15). The high degree of reactivity was primarily attributed to the high organic sulfur and reactive maceral (vitrinite and exinite) content of Wyo-3 coal. Coal samples were dried to less than 1.0 wt% moisture content before use.

Two shale oil samples were used in low severity liquefaction co-processing runs. Solvent A-5 was a full boiling range sample of shale oil obtained from the Western Research Institute (formerly the Laramie Energy Technology Center of the Department of Energy). This sample was produced from thermal retorting of medium grade (29 gal/ton) Colorado oil shale. Solvent A-6 was prepared by mildly hydrotreating a portion of sample A-5 in a two liter batch Autoclave Magnedrive II reactor at 650°F for one hour with an initial cold hydrogen pressure of 2000 psig. Nalco 477 cobalt molybdate catalyst was used to hydrotreat the shale oil. Catalyst samples were thermally activated at 1000°F for two hours in a muffle furnace prior to use. Approximately 0.6 wt% hydrogen was consumed by the shale oil during hydrotreating. Properties of shale oil samples A-5 and A-6 are presented in Table II. Approximately 50 wt% of the nitrogen in these samples existed in quinoline-type or hydroquinoline-type molecular structures.

Runs were carried out in a 60 cm³ stirred microautoclave reactor system designed and constructed at the University of Wyoming. This reactor was similar to larger Autoclave batch reactors except that heating was accomplished with an external high temperature furnace. At the end of each run, the reactor and its contents were quenched with an icewater batch. This reactor system provided the benefits of small tubing bomb reactors [quick heatup (~1 min. from room temperature to 650°F) and cooldown (~30 sec. back to room temperature)], while at the same time insuring sufficient mechanical agitation of the reactants with an Autoclave Magnedrive II stirring assembly to minimize hydrogen mass transfer effects. The system was also designed so that the reactor pressure was very nearly constant throughout an experiment. Two iron-constantan thermocouples attached to a Fluke 2175A digital thermometer were used for temperature measurements. One thermocouple measured the temperature of the reactor contents, while the other measured the temperature of the reactor wall. Reactor pressure was monitored using a 0 - 5000 psi Marsh pressure gauge.

In these runs, carbon monoxide and water were used as reducing agent, with hydrogen being produced via the aqueous phase water-gas shift reaction. Reaction conditions were studied in the range: 600-650°F

reaction temperature, 1000-1500 psig initial cold carbon monoxide pressure, and 15-60 minutes reaction time. Distilled water is an amount equal to 50 wt% of the dry feed coal was charged to each reactor run. Iron sulfate (5 wt% dry feed coal) was used as a disposable catalyst.

Gaseous products were analyzed using gas chromatography. Water and distillate yields were measured by distilling portions of the combined liquid-solid product mixture to an 850°F endpoint in a micro-distillation apparatus. Additional portions of the liquid-solid product mixture were extracted in a Soxhlet extraction apparatus using cyclohexane, toluene, and pyridine. Details of the experimental procedures used in this work have been reported (9).

RESULTS AND DISCUSSION

Using data collected with the analytical procedures described, detailed yield and conversion results were computed for each liquefaction co-processing run. Details of the computational methods used in this study have been described previously (9). For purposes of the present discussion, process performance will be monitored using the following two parameters: C_4 -850°F distillate yield (wt% MAF coal basis), and pyridine conversion (wt% MAF basis). Pyridine conversion is defined as a measure of the extent of conversion of all feeds (coal and non-coal-derived heavy oil) to pyridine soluble products. However, since both A-5 and A-6 shale oil samples were completely soluble in pyridine and negligible coking of the shale oil occurred at low severity reaction conditions, pyridine conversion values reported in this paper are direct measures of the extent of coal conversion in the co-processing runs.

Effect of Shale Oil Prehydrotreatment

Figure 1 shows distillate yield results from co-processing runs completed using Wyo-3 coal and either A-5 or A-6 shale oil at 600°F and 1500 psig initial cold CO pressure. This data clearly shows that mild hydrotreatment of the shale oil greatly enhances co-processing performance. Coal conversion also increased significantly when A-6 shale oil was used in place of A-5 shale oil. Distillate yields of over 85 wt% MAF coal (58 wt% MAF coal and 850°F+ shale oil) and pyridine soluble coal conversions of nearly 60 wt% MAF basis were obtained with A-6. Previous high severity co-processing studies using Wyo-3 and A-6 also demonstrated the beneficial effect of prehydrotreatment. The enhancement at low severity conditions can be attributed to: 1) increased hydrogen donor ability of the hydrotreated shale oils and 2) increased concentration of partially hydrogenated basic nitrogen compounds such as tetrahydroquinoline and piperidinopyridine in the shale oil. These compounds are known to promote coal dissolution and catalyze the aqueous phase water-gas shift reaction.

Effect of Reaction Temperature

Figures 2 and 3 present yield and conversion results for co-processing runs completed with Wyo-3 and A-6 at 600°F and 650°F. These data show that process performance improved at lower reaction temperature. This effect can be at least partially attributed to the favorable thermodynamic equilibrium of the water-gas shift reaction at lower temperatures.

Effect of Initial Carbon Monoxide Pressure

The effect of varying the initial CO pressure is illustrated in Figure 4. At 600°F reaction temperature, increasing the CO pressure from 1000 to 1500 psig more than doubled the distillate yield over the entire range of reaction times studied. These data indicate that relatively high pressure is required to achieve sufficient CO solubility in the aqueous phase for the water-gas shift reaction to proceed at a satisfactory rate.

Results from Blank A-6 Shale Oil Runs

In an attempt to estimate the amounts of distillate derived from coal and from shale oil, several blank shale oil runs (no coal added) were completed. Results from both high severity and low severity blank runs are shown in Figure 5. These data were then used to estimate the amount of distillate attributable to the shale oil feed in each co-processing run. Estimates of the coal-derived distillate production were computed by assuming that half of the total coal-derived cyclohexane soluble product was distillate. Results of these calculations are shown in Figure 6. Both low severity and high severity runs are included in this figure for comparison purposes. In each co-processing run, additional distillate in excess of that predicted by the blank shale oil runs was obtained. Thus, it appears likely that the reactivity of shale oil residuum towards distillate production is enhanced in the presence of coal or primary coal-derived products.

CONCLUSIONS

A series of low severity liquefaction co-processing runs has been completed using Wyodak subbituminous coal and two shale oil samples. Results indicated that prehydrotreatment of the shale oil, lower reaction temperature, and higher initial CO pressure all contributed to enhanced process performance. Distillate yields in excess of 85 wt% MAF coal were obtained at 600°F, 1500 psig CO pressure, and 60 minute reaction time. Results from blank shale oil experiments suggested that overall distillate yield could be maximized by co-processing coal and shale oil rather than processing the two feeds separately.

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Table I

Ultimate Analysis of Wyodak
Subbituminous Coal Wyo-3

Ultimate Analysis, wt% dry basis

Carbon	58.2
Hydrogen	4.3
Nitrogen	0.8
Sulfur	2.9
Sulfate	0.8
Pyrite	0.9
Organic	1.2
Oxygen (difference)	13.9
Ash	19.9

Table II
Properties of Shale Oil Samples

Sample	<u>A-5</u>	<u>A-6</u>
Wt% Distilled		
Water	0.7	0.1
350°F	4.2	10.3
350°F-500°F	9.6	18.3
500°F-650°F	18.8	22.5
650°F-850°F	39.0	29.8
850°F+	27.7	19.0
Ultimate Analysis, wt% dry basis		
Carbon	83.3	84.7
Hydrogen	12.1	12.9
Nitrogen	1.4	1.2
Sulfur	0.5	0.4
Oxygen (difference)	2.7	0.8
Ash	0.0	0.0

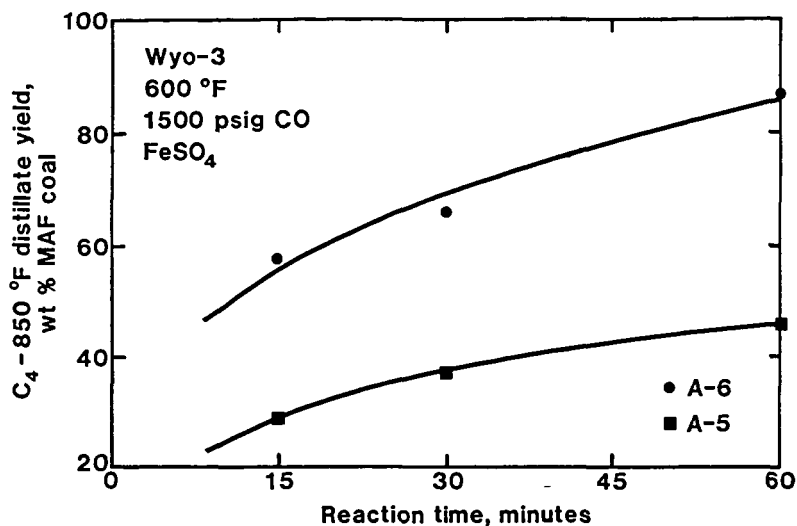


Figure 1. Distillate Yield as a Function of Reaction Time and Shale Oil Feed

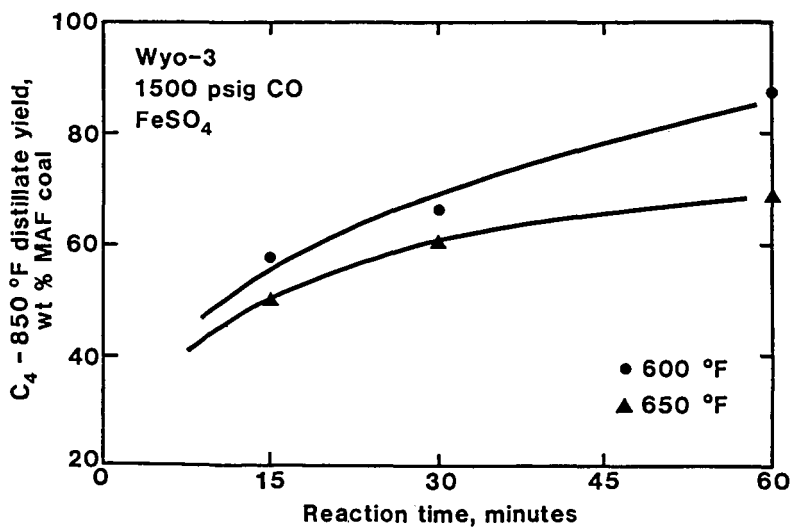


Figure 2. Distillate Yield as a Function of Reaction Time and Temperature

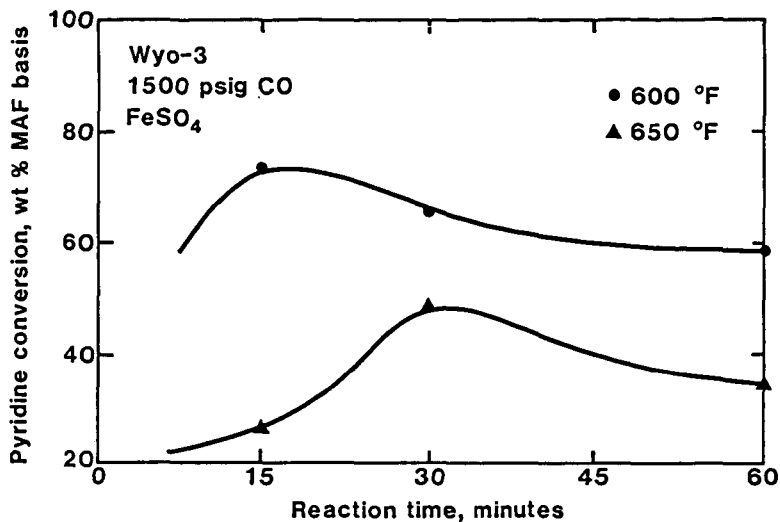


Figure 3. Pyridine Conversion as a Function of Reaction Time and Temperature

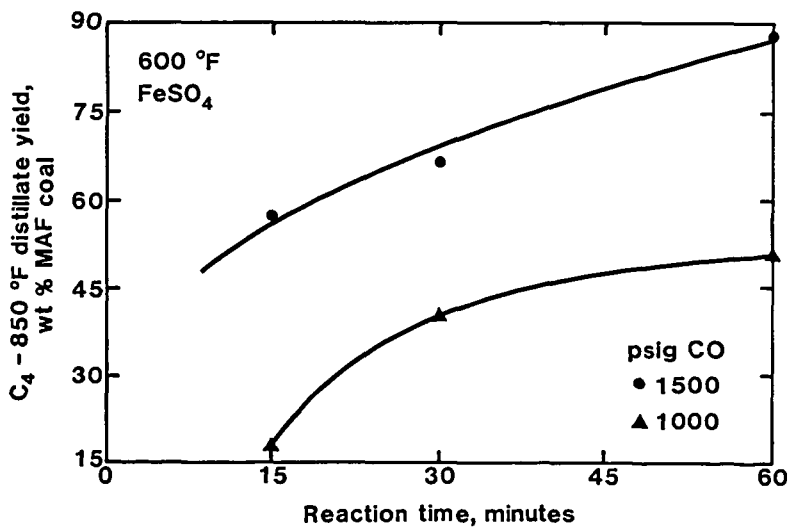


Figure 4. Distillate Yield as a Function of Reaction Time and CO Pressure

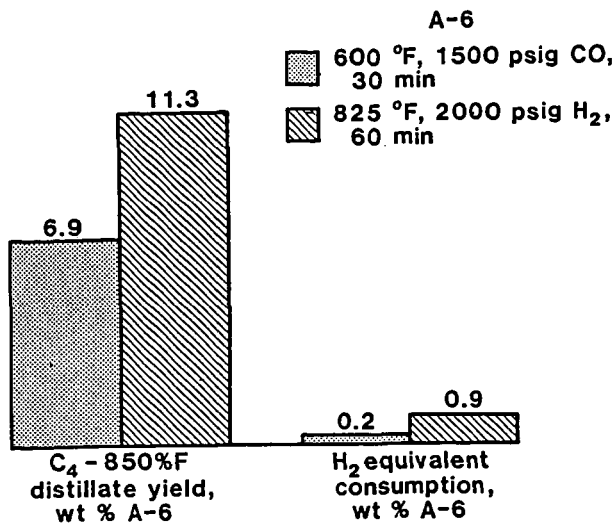


Figure 5. Results from Blank Shale Oil Runs at Low and High Severity Reaction Conditions

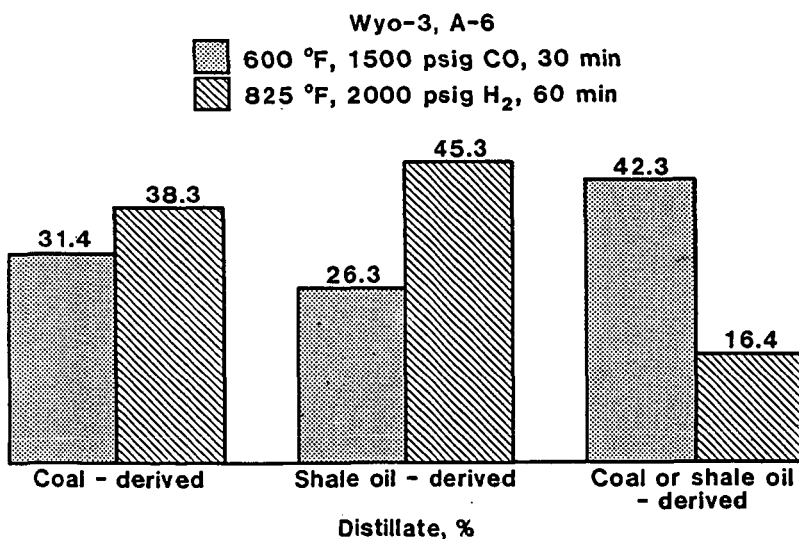


Figure 6. Estimated Distribution of Distillate Production from Wyo-3 Coal and A-6 Shale Oil at Low and High Severity Reaction Conditions